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Dynamic Testing of Gasifier Refractory

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ABSTRACT

As DOE continues to advance new power systems, materials issues are often pivotal in determining the ultimate efficiency that can be reached in the system. Refractory performance in slagging gasification represents one of these issues. The University of North Dakota (UND) Chemical Engineering Department in conjunction with the UND Energy & Environmental Research Center (EERC) have initiated a program to thoroughly examine the combined chemical (reaction and phase change) and physical (erosion) effects experienced by a variety of refractory materials during both normal operation and thermal cycling under slagging coal gasification conditions. The goal of this work is to devise a mechanism of refractory loss under these conditions.

The focus of the proposed work is to test the corrosion resistance of commercially available refractories to flowing coal slag, and propose the mechanisms of corrosion for the conditions studied. Corrosion is the degradation of material surfaces or grain boundaries by chemical reactions with melts, liquids, or gases, causing loss of material and consequently a decrease in strength of the structure. In order to develop methods of reducing corrosion, the microstructure that is attacked must be identified along with the mechanism and rates of attack. Once these are identified, methods for reducing corrosion rates can be developed.

The work will take advantage of equipment and experimental techniques developed at the EERC under funding from several DOE programs. The controlled-atmospheric dynamic corrodent application furnace (CADCAF) will be utilized to simulate refractory/slag interactions under dynamic conditions that more realistically simulate the environment in a slagging coal gasifier than any of the static tests used previously by refractory manufacturers and researchers.

To date, efforts have focused on final shakedown of the CADCAF and obtaining representative samples of slag and refractory for testing.

DYNAMIC TESTING OF GASIFIER REFRACTORY

INTRODUCTION

The recent events in California provide a strong impetus to the Vision 21 program being developed by DOE. While the rolling blackouts can be attributed primarily to shortsightedness in California's deregulation policy, evidence of the shrinking power reserves, and the need to build new electricity generation plants, is apparent. Coal gasification integrated into the energy cycle of a power plant is one of the more promising technologies that is capable of meeting the demand for new generating capacity while addressing the strong environmental concerns that have been delaying the construction of new power plants.

As DOE continues to advance new power systems, materials issues are often pivotal in determining the ultimate efficiency that can be reached in the system. A specific example is the need for refractories able to withstand both oxidizing and reducing environments, with high temperature strength, and the ability to resist corrosion by flowing slag and rapid thermal cycling. The University of North Dakota (UND) Chemical Engineering Department in conjunction with the UND Energy & Environmental Research Center (EERC) has undertaken a study to thoroughly examine the combined chemical (reaction and phase change) and physical (erosion) effects experienced by a variety of refractory materials during both normal operation and thermal cycling under slagging coal gasification conditions. The goal of this work is to devise a mechanism of refractory loss under these conditions.

The work takes advantage of equipment and experimental techniques developed at the EERC under funding from several DOE programs. The controlled-atmospheric dynamic corrodent application furnace (CADCAF) will be utilized to simulate refractory/slag interactions under dynamic conditions that more realistically simulate the environment in a slagging coal gasifier than any of the static tests used previously by refractory manufacturers and researchers. The CADCAF, along with advanced analytical techniques, provide the team with unique tools to evaluate the refractory problems facing the gasifier-based advanced power systems being developed under Vision 21.

PROBLEM DEFINITION

Corrosion is the degradation of material surfaces or grain boundaries by chemical reactions with melts, liquids, or gases, causing loss of material and consequently a decrease in strength of the structure. In order to develop methods of reducing corrosion, the microstructure that is attacked must be identified along with the mechanism and rates of attack. Once these are identified, methods for reducing corrosion rates can be developed.

Refractory corrosion is of concern in gasification systems for several reasons. Gasifiers, especially those that remove the ash in the form of a molten slag, operate at high temperatures over 1400C. At these high temperatures, chemical equilibria can become favorable for the interaction/reaction of the ash material from the fuel with the refractory, and the liquid state of the slag assures rapid reaction. The reduced species that are typically present in gasifier slags are typically more corrosive than their oxidized forms, and cause the slag to become liquid at lower temperatures than typically seen in combustion systems. To complicate matters, a commercial gasification system can experience sudden changes in temperature, subjecting the refractory material to thermal shock, and can switch from reducing to oxidizing as a result of process upsets.

The fact that the slag is liquid not only causes high reaction rates with the refractory because of the rapid transport of slag corrodents to the refractory surface, but also leads to the penetration of the slag into the refractory, even those that are nonporous, setting up the potential for chemical reactions below the surface of the material. These reactions can result in the dissolution of the refractory material, in particular, the cement below the surface. Often of more importance though, is the crystallization of secondary species, often with higher specific volumes than the original material, which leads to expansion and bursting of the refractory.

The physical properties of the slag in a coal gasification system are functions of the characteristics of the fuel being utilized. One concern is the viscosity of the slag at operating temperatures in the gasifier. Slags of low viscosity will flow more easily and more readily penetrate the refractory material. In addition, a low viscosity material that readily flows will continually and rapidly remove any corrosion products formed at the surface of the refractory, and replace them with fresh slag. Therefore, rather than coming to an equilibrium, the continuously running slag continues to reestablish the chemical driving force required for rapid and severe corrosion. A second expectation with low viscosity slags is the formation of relatively thin layers of slag. While a thick slag may be able to "insulate" the refractory from the gas phase species, with a thin layer of slag the gaseous environment in the gasifier is able to participate in the chemical reactions between the refractory and the slag.

The reactivity of the ash with the refractory, and the proper selection of refractory material will also be impacted by the chemical composition of the ash. On a broad sense, differences in reactivity can be expected between a basic and an acidic ash. Other more subtle differences will manifest themselves as the both the elemental and mineral composition vary within these two broad classifications.

Experimental data for modeling refractory materials in coal gasification systems is scant. While some limited work has been performed at high temperature slagging combustion conditions, much of the limited research performed for slagging gasifiers is proprietary. Information obtained from the DOE programs such as Combustion 2000 can and should be utilized as a starting point for developing experimental methods and proposing mechanisms for refractory corrosion in gasification systems.

Fortunately, the high temperatures under investigation add some simplification to the understanding of ash/refractory interactions. While ash is typically a very nonhomogeneous material, the molten slag that is formed at the expected temperatures in the gasifier will be homogeneous. In addition, due to the high temperatures, it is expected that the system will be at thermodynamic equilibrium. This implies that existing thermochemical equilibrium models such as the Facility for Chemical Analysis of Thermodynamics, or FACT code, could be utilized to model behavior in the gasifier. While FACT and other models may be a part of the tools used to investigate the problem, they are often limited in their use because the current thermodynamic data bases do not include all of the species required to adequately model the complex system that exists in the gasifier. However, knowing that the system is homogenous and at equilibrium does allow the use of other analytical methods, such as heated stage x-ray diffraction to help define the system.

APPROACH

The focus of the work is to test the corrosion resistance of commercially available refractories to flowing coal slag, and propose the mechanisms of corrosion for the conditions studied. The focus will then shift to improving the corrosion resistance of the near surface of the grains and bond phase between grains, since bonding phases normally have a lower melting point and lower corrosion resistance than does the bulk of the material. Other tests may focus on the use of slag additives to decrease the corrosivity of the slag itself.

The primary tool that will be used to simulate the interaction of the ash generated slag and refractory is the controlled-atmosphere dynamic corrodent application furnace (CADCAF). It was designed to simulate conditions of dynamic corrosion on the vertical wall of a refractory-lined coal gasifier or glass or steel industry furnace, under controlled atmospheric conditions. The CADCAF, shown schematically in Figure 1 has the capability of testing two refractory test blocks simultaneously, up to a maximum of 1600°C. Two corrodent injector feed ports and a single view port are located on the removable portion of the top of the furnace. Corrodents may consist of any granular material such as coal or steel slag, or glass cullet. An exit port for the spent corrodent material is located at the bottom of the furnace. The molten spent corrodent material will exit the furnace through a heated ceramic tube into a removable refractory lined catch pot and be available for post-test analysis.

The powder feeder is a precise low-rate volumetric feeder with full hopper agitation made of 316 stainless steel material. The feeder needs to be gas tight to several inches of water to allow the system to be completely sealed to prevent the reactive gases to escape or oxygen to enter the system [current work is focused on sealing of the system]. For any given test, a preselected gas mixture will be introduced through a gas inlet valve located on the side of the corrodent hopper. The gas will mix with the corrodent material, then enter the furnace through the feed injectors. It exits the system through a gas outlet vent located on one side of the slag catch pot, then exhausted through the fume hood.

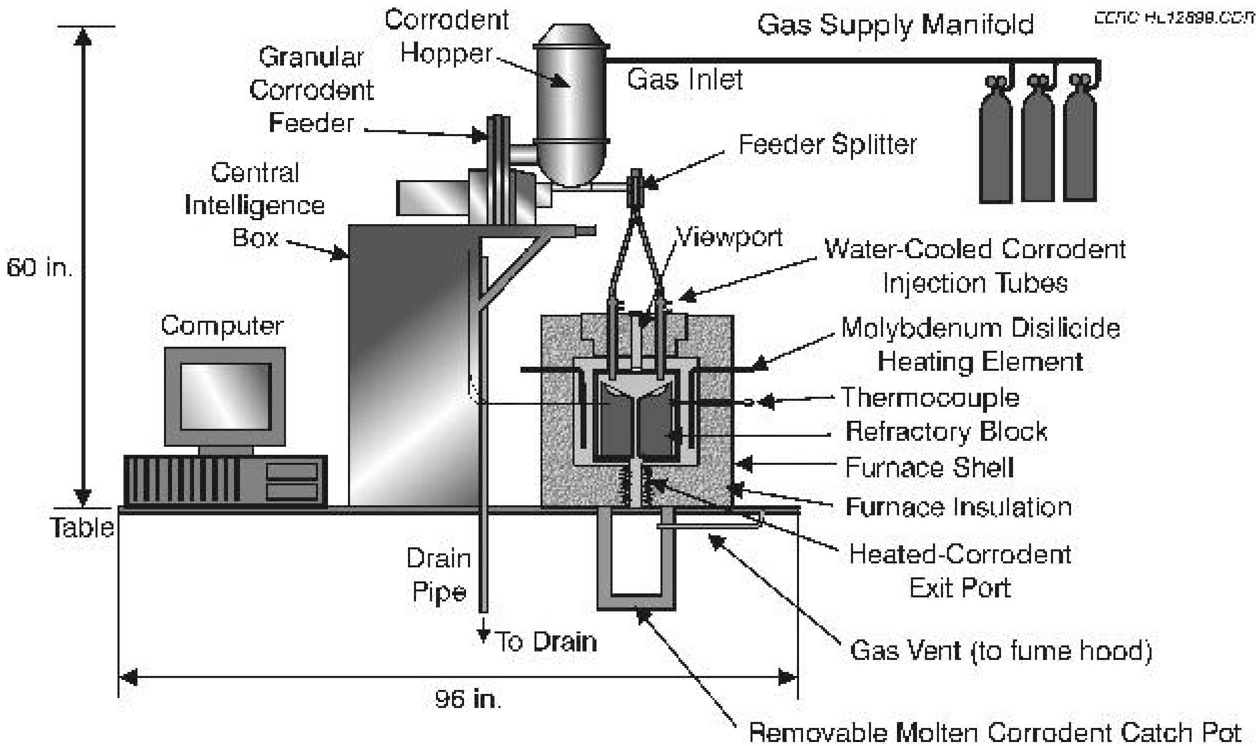

Figure 1. Schematic of the inside of the CADCAF with refractory blocks in place.

Results from these dynamic experiments will be evaluated using several techniques to analyze the combined impacts of ash chemistry and refractory composition on refractory wear. Exposed refractory samples will be evaluated to determine the penetration depth and surface recession as a first estimate of the refractories resistance to attack. Scanning electron microscopy (SEM) will be used to determine if the primary attack was against the cement material or the aggregate. The SEM will be used to map the chemical composition of the exposed slag as a function of depth. These maps will help determine the penetration of various ash components into the refractory and/or the leaching of materials from the refractory. Selective penetration or leaching of specific elements will be important in understanding the mechanisms of refractory attack.

Another analytical tool that will be used in this study is heated-stage x-ray diffraction (XRD). Samples of slag prior to exposure to the refractory, and of the material after exposure (containing corrosion products), will be analyzed. The heated-stage XRD allows the user to identify the temperature at which various crystalline phases will form from the glass phase. Identification of the type of crystalline material that may be formed and under what conditions it forms will provide valuable insights into understanding methods by which additives to the slag or the refractory can help reduce corrosion rates.

The effect of process variables on surface recession of the refractories be investigated using the CADCAF. For example, small changes in temperature can significantly effect the viscosity of the flowing slag. These experiments will help evaluate the impact of slag viscosity on the mechanisms of refractory wear. Secondary effects of temperature that will also be considered is the crystallization of certain species from the slag as the temperature is reduced, and changes in the kinetics and chemical equilibrium with temperature variations.

CADCAF tests will be performed with both acidic and basic coal ashes. Under testing performed for Combustion 2000, basic slags were found to be more corrosive to certain refractories than acidic slags. With castable alumina refractories, the basic slags penetrated the refractory and formed secondary crystallization products that expanded and caused the refractory to burst. Therefore, the ash materials chosen for testing will include at least two bituminous and two low-rank (subbituminous or lignitic) coals. Selection of test materials(coals) will be made to compliment DOE's existing data base.

Another approach that will be used to both help elucidate mechanisms and to assist in the development of more corrosion resistant refractories is to investigate a variety of refractory compositions. Phase diagrams will be utilized to identify stable high-melting material that could modify the bonding phase of the refractory. Mechanisms of reducing corrosion to be investigated include the formation of corrosion-resistant surface layers and increased sintering to raise strength and seal pores to reduce slag penetration.

Slag additives will be investigated as methods of altering the chemical and/or physical properties of the slag. Results of experiments under combustion conditions indicate that the flowing slag becomes significantly less corrosive as the slag dissolves some of the refractory. This may be due to changes in the slag viscosity or by changing the chemical composition of the slag so that it becomes saturated with the chemical species found in the refractory. As the saturation point is approached, dissolution rates would be expected to decrease markedly.

Thermal shock is can also play a critical role in refractory wear. The potential impact of thermal cycling will be evaluated using two different approaches. The first makes use of the penetration and compositional data obtain during CADCAF tests performed at a constant temperature. The intent is to determine the type and amount of slag penetration and reaction that has occurred with a given slag/refractory composition. Using this information and data generated from the heated XRD experiments, the potential to form crystallization products on cooling that will expand and cause the refractory to burst will be evaluated. A second technique will be to cycle the temperature of the CADCAF, allowing the refractory to freeze and remelt over several cycles and comparing these results to those obtained from the standard tests performed under constant temperature.

SCOPE OF WORK AND STATUS

The primary objective of the proposed work is to perform well defined experiments that will provide insight and understanding into the performance of refractory materials under slagging gasification conditions that will lead to the development of mechanisms of refractory loss under gasification conditions. This objective will be met by simulating ash/refractory interactions using a bench-scale test apparatus, followed by analysis of the corroded refractory and slag using advanced analytical techniques.

Task 1 - Selection of Materials for Initial Screening [on-going]

The initial tests will be performed using two coal ashes and five different refractory materials. Ash from a bituminous and a low-rank coal will be selected to allow a comparison between an acidic and basic ash.

The objectives of the current project were discussed with plant personnel at the Tampa Electric Polk Power Station. Samples of slag and refractory were requested for testing in the CADCAF. A 55 gallon drum of gasifier slag along with several refractory bricks of the type that they use in the gasifier have been received. The slag has been dried and sieved to the size needed for our flowing slag corrosion tests.

Tampa Electric personnel have also requested that we test bricks of refractory made by Salazar and Sons which they are contemplating using in the gasifier. Paul Salazar visited UND to discuss the testing and provided a sample brick, sized to our specifications, of a vibratable SiC/Al_2O_3 material that Salazar and Sons is proposing for the Polk gasifier. A slag resistant dense coating material that will be used to provide a gas-tight seal in the sample crucible of the Controlled Atmosphere Dynamic Corrodent Application Furnace (CADCAF) was also provided by Salazar and Sons.

Discussions have also been ongoing with personnel at the Albany Research Center. We have discussed testing experimental refractory(s) developed at the Albany Research Center as a part of this program. The Albany Research Center has expressed willingness to machine the refractory material to the required shape for testing in the CADCAF. The team from UND will maintain dialog with the Albany Research Center as work progresses to provide an additional resource for evaluating program results.

Task 2 - Broad Brush Screening CADCAF Tests [on-going]

The CADCAF was designed and constructed initiated under previous DOE funding. All of the major components had been purchases, manufactured, and installed under the previous program. Since the start of the current project, efforts have focused on finalizing construction of the CADCAF. These final efforts focused primarily on issues related to sealing the CADCAF system, and dealing with a variety of safety related issues. Currently, the CADCAF system is 95% complete. The final equipment required to address the sealing and safety issues have been purchased, and require only the installation of computer monitoring modules and sealing of gas leaks before shakedown and screening testing can begin.

Ten tests are planned using the CADCAF - 2 ashes with 5 different refractories. Test durations are expected to be between 50 and 100 hours. Following each test, the refractory blocks will be analyzed macroscopically and microscopically using the SEM to measure ash penetration and refractory wear. Elemental mapping will be performed of the refractory material to determine which elements penetrated into the refractory and to what depth. The slag collected during the tests will be analyzed for bulk composition and with heated-stage XRD to evaluate the glass and crystalline phases present in the slag. In addition, the heated-stage XRD will be used to determine the crystallization behavior of the slag and indicate possible additives that can be used to reduce the corrosivity of the slag. Viscosity versus temperature measurements will also be employed to suggest appropriate additives and critical slag temperatures that affect the corrosivity of the slag. These analytical techniques will be used to analyze samples generated from some or all experimental work performed during this program (Tasks 1-5).

Task 3 - Directed CADCAF Testing

Results from Task 2 are expected to give an indication of slag/refractory combinations that exhibit different levels of refractory wear, penetration, and crystallization. Some preliminary hypotheses will be made based on Task 2 results. Starting from these hypotheses, additional tests (up to 10) will be planned to help prove, disprove, and/or expand on the preliminary findings. These tests are likely to include different ash and refractory types and/or additives which will be carefully selected to help pinpoint corrosion mechanisms.

The same analytical techniques outlined in Task 2 will be used to analyze the samples generated in Task 3. Based on Task 3 results, revised hypotheses of corrosion mechanisms and ways of reducing or preventing corrosion will be developed.

Task 4 - Thermal Shock

Testing during Task 4 will investigate the effect of temperature cycling on refractory materials. The first series of corrosion tests to be performed will be isothermal at two or three different temperatures to investigate the indirect impacts of temperature on refractory wear. These will include impacts of slag viscosity, crystallization, and possibly reaction kinetics.

The CADCAF will also be operated in a non isothermal mode to investigate thermal shock. In this mode, the CADCAF will be operated at a high temperature for a preset period of time and allowed to cool to the point where the slag freezes. The CADCAF will be reheated to the point of a flowing slag, held at that temperature for a preset period of time, and again cooled. This will be repeated for 5 cycles. Two experiments will be performed with a basic and acidic coal ash. The analysis of these samples will focus on differences between these samples and those generated from the standard isothermal tests.

This type of thermal shock experimentation has not been previously performed, so it is expected that some development work will be required. Ash and refractory types will be selected based on results from the previous tasks.

Task 5 - Development of Mechanisms

The primary objective of the work is to develop an understanding of ash/refractory interactions that will lead to the development of mechanisms that describe the interactions of slag (coal-ash) and refractory. Although listed as the last task, the development of mechanisms will be a consistent theme throughout this project. Mechanisms will be hypothesized early in the program, and will be utilized to direct the testing during the program. The proposed mechanism will be constantly updated as new data is generated. Likewise, the latest hypothesis will be used to determine the next series of tests. At the end of the Task 5, final mechanisms that describe the behavior noted during the program will be proposed. Additional experimental work will be performed as required to verify assumptions.

Throughout the test program, the project team will maintain constant communication with refractory vendors to ensure refractory material being investigated represent commercial and experimental formulations that are realistic for commercial application. This direct communication will also promote timely dissemination of results. Results from the program will also be presented at the annual DOE Contractor's Review Meeting.

DELIVERABLES

This program was originally designed for a doctoral student or two master's students, with additional work for an undergraduate student. It was assumed that the doctoral/master's student would spend a significant portion of the first year becoming familiar with the project and performing a detailed review of the literature. It was also expected that the final construction and shakedown activities would be completed prior to the start of this project. Therefore, the first year's experimental work was planned accordingly. However, since the CADCAF was not operational at the start of the current project, considerable time has been spent addressing the sealing and safety issues discussed previously. This has set the project approximately 6 months behind schedule.

Current plans are to complete the screening test and begin the directed CADCAF testing during the second year and focus on thermal shock testing, mechanism development and thesis/dissertation preparation during the third year. Limited experimentation will occur during the third year when required to substantiate assumptions. Revised project milestones are listed in Table 1.

Table 1. Project Milestones

Activity	Months from Contract Award
Selection of Materials for Testing	6
Literature Review and Screening Tests	(12)* 18
Contractor's Review Meeting	12

Activity	Months from Contract Award
Directed CADCAF Testing	(21) 24
Thermal Shock Tests	(24) 27
Contractor's Review Meeting	24
Mechanism Development	32
Peer Review Meeting	34
Final Project Report	36

* Original schedule

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